PREPARATION AND CHARACTERISATION OF METALLIC THIN FILMS FOR ELECTROLUMINESCENT DEVICES BASED ON POROUS SILICON

Irina Kleps, Anca Angelescu and Mihaela Miu
National Institute for Research and Development in Microtechnologies (IMT), P.O.Box 38-160, Bucharest, Romania, fax: 40.1.2307519, tel.: 40.1.2313040/33, e-mail: <irinak@imt.ro>

Abstract
For porous silicon (PS) electroluminescent (EL) devices, metallisation is a key process. The state of the art of the main preparation methods of thin metallic films used in PS EL devices is described. Experimental results concerning the structural and electrical characterisation of the metal/PS/p-Si structures are also presented. Different materials, like Au, In, Au-In, In-Sn, Al, etc., in a variety of preparation conditions were used as a solid-state contact on the PS layers. The luminescent properties of these structures were checked after metallic layer deposition by exciting the samples with an UV lamp. It is known that the transparency of a thin layer of 15 nm thickness is 60% or lower, finally only the luminescent structures were evaluated. Scanning Force Microscopy was used to investigate the film morphology; from the I-V characteristics of the metal/PS/p-Si structures it was determined: n<3, series resistance <500 Ω, low values for contact resistance. The structures with low series resistance values, present the EL properties at lower value of the applied voltage, and are indicated for LED on PS type.

1. Introduction

The porous silicon (PS), composed by Si nanocrystallites, prepared by the electrochemical etching opened the way to Si optoelectronic devices fabrication because it shows strong visible photoluminescence (PL) at room temperature [1]. Since 1991 many EL devices have been realised [2-5]. Most of them are made in a two step process: anodisation and deposition of a contact layer. Very thin metallic layers are often used as a solid contact on PS electroluminescent devices.

Metallisation is a key process with several requirements as follows: (i) it must ensure a good electrical contact between the metal layer and PS; (ii) the metal layer must be thin, to transmit as much light as possible from the PS beneath; (iii) there must be good control over the penetration depth of the metal into the pores.

The aim of this paper is to investigate the properties of different metallic contacts on porous silicon layers related to the preparation methods.

2. State of the art regarding the metallic thin films contacts for PS electroluminescent devices

EL devices with different structures and characteristics have been reported. A very comprehensive study regarding different PS EL device structures was made by T. I. Cox [6]. So, there are described the following types of PS EL devices: (i) with top

G.M. Chow et al. (eds.), Nanostructured Films and Coatings, 337–345.

contact on PS single layer (ii) p-n porosified junction, (iii) PS layer impregnated with another material, (iv) PS oxidised layer, (v) PS layer contacted by a non-porous semiconductor, (vi) PS layer in a microcavity, (vii) PS formed by stain etching. These varieties in EL device technologies make the comparison between the device characteristics more difficult. One of the major problems in the implementation of PS layers as solid-state light-emitting elements is the formation of a top electrode on the PS surface. Until now, different preparation methods for solid contact on PS EL device have been reported. An important drawback of the existing methods is related to the high electrical resistance of the contacts that require working voltages as high as 10-30 V, and result in a low quantum efficiency of the light emitting structures. The high value of the contact resistance is due to poor penetration of the deposited material into the PS pores. Additional problems of this poor contact are related to the insufficient adhesion of the deposited material.

The first EL devices were made by porosification of n- [2] or p- [3, 7] type Si with a top contact of either gold or indium tin oxide. The reported device [2] emitted red light at 200 V with a low efficiency. Later variants have threshold voltages as low as 1.35 V [8] and efficiency up to 0.05 % [9]. In any case, there are many factors which depend on the EL device properties. The efficiency of the PS EL devices is usually low (10^{-3} %), although some groups have reported lower values. The effect of using different metals [10] to contact PS layer produced by anodising under UV light has been studied. The peak wavelengths depend on the metal contact, and can be varied in the range 455 nm (indium) to 700 nm (antimony). One group has obtained a structure in which optically transmitting windows are produced in an opaque aluminium contact layer by anodically oxidising the aluminium to form transparent aluminium oxide [11-15]. The synthesis of the main PS solid contact preparation methods is presented below.

2.1. Physical vapour deposition (PVD) methods: thermal heating/electron beam evaporation and sputtering

The most usual methods for PS EL devices contact fabrication are evaporation and electron beam sputtering. In order to obtain a better penetration of the metallic layer in PS pores, the dynamic deposition regime at an angle of 30^0 is usually used for PS solid contacts.

It is generally known that PS fabricated by low-current density (1-100 mA/cm^2) anodisation has a spongelike structure with low carrier mobility [16]. For electroluminescent device applications, a sufficient electrode contact over the inside of PS, such as aqueous electrolyte contact [17], is necessary. However, these contacts are difficult to achieve by normal evaporation techniques, so that, the electrode-contact area is limited to the top of the surface, and the rest of the PS layer acts only as a resistor in such kind of diodes. Moreover, the large inner surface of the PS layer interacts with the air, and the oxidised PS causes the increase of the series resistance and the instability of the devices. The PS solid contact can be a single metal such as Au, Cr, Al, or can be formed by successive layers In/Au, In/Sn, Sn/Au or by the respective alloys. In the case of In-Au contact on PS, the device EL increase 150 times, and the emission light peak shifts towards lower wave numbers. In addition, the efficiency increases twice [10,18-19].

2.2. Electroplating method

In order to avoid the PS deterioration of luminescence properties, it is indicated to use a method to fill the pores with some material, such as the electrochemical processing. Metals such as gold, indium, or polymers such as polyaniline, polypyrrole, polyfuran and polythiophene have been deposited on PS as solid contacts.

This process is conducted in a liquid solution which penetrates over the entire depth of the pores and is stimulated by an electric field, thus making it possible to form a contact layer at the pore bottoms where the maximum electric field is localized. The conducting material is not required to completely fill the inner pore because this could short circuit the active layer. The best solution to increase the light device efficiency is to cover the Si skeleton walls with a very thin conductive layer in order to ensure the contact transparency. There are only a few published papers [20] on this subject because it is very difficult to approximate the PS area and the cathode/anode current density, in order to cover the Si skeleton walls and not to fill the pores.

2.3. Chemical vapour infiltration and deposition (CVID)

In this process a PS substrate is placed in a vacuum and is warmed. The process is monitored in such a way that the vapour precursor molecules have enough time to penetrate and decompose inside the PS pores. The vapour which has not penetrated into the pores will decompose above the warmed PS, resulting in a metal cap over the PS substrate surface. By this method, Co was deposited on and in a porous silicon layer using deuterated cobalt carbonyl hydride $DCo(CO)_4$. [21].

This precursor is unstable, and below 22^0C decomposes and reacts with Si-H bonds on the pore walls to give Si-Co bonds.

3. Experimental data

Different materials such as Au, In, Au-In, Sn-Au, In-Sn, Al Cr, Ni, Mo, Ti, doped and undoped polypyrrole, obtained in a variety of preparation conditions have been used as solid-state contact on the PS layers for EL device applications (Table 1).

The luminescence from the metal/PS structures was observed by exciting the samples with an UV lamp. Only the properties of the luminescent structures were determined. Metal/PS morphology was investigated by scanning force microscopy (SFM) [22]. UV-visible spectra of the metals used as solid contact on PS were determined. The electrical characterisation of the metal/PS/p-Si structures was performed by current-voltage (I-V) measuring using a computer-interfaced Keithley apparatus. The structures were measured under forward (positive bias applied to p-Si) and reverse bias conditions, at room temperature.

3.1. Solid contacts preparation

The starting material was crystalline p-Si wafers (100) oriented and with 6-10 Ωcm resistivity. The PS layers formation was performed in an electrochemical process. The concentrations of the ethanoic HF solutions were 12% and the current densities 10 mA/cm^2, in order to obtain 80% porous silicon porosity [23].

Table 1. Experimental data

No.	Solid contact layer			Luminescent properties of the contact/PS/Si structures	Electrical properties of the contact/PS/Si structures	
	Preparation	Thickness (nm)	Transmission (%) $\lambda = 660$ nm		Rs (kΩ)	φB (eV)
1.	Al, electron beam sputtering 10^{-6} torr, 1-2 A/sec	10 20	18 12	weak very weak	0.25	0.83-0.89
2.	Au, electron beam sputtering, 10^{-6} torr	10	47	very good	0.45	0.79-0.84
3.	Cr, electron beam sputtering 10^{-6} torr	6 10 20	43.5 30.5 14.8	very good good weak	-	-
4.	Ti vacuum evaporation $5x10^{-6}$ Torr, 10 A/sec	10	38	good	-	-
5.	Ni vacuum evaporation $5x10^{-6}$ Torr, 10 A/sec	10	32	good	-	-
6.	Au vacuum evaporation $5x10^{-6}$ Torr, 10 A/sec	10	46	very good	-	-
7.	Cr vacuum evaporation $5x10^{-6}$ Torr, 10 A/sec	10	31	good	-	-
8.	Mo vacuum evaporation $5x10^{-6}$ Torr, 10 A/sec	10	30	good	-	-
9.	In-Sn (9:1) vacuum evaporation, 10^{-6} Torr, air annealing at 120°C	100	35	good	0.38	0.9
10.	In-Au (1:1) vacuum evaporation, 10^{-6} Torr, air annealing at 120°C	20	18	weak	25	0.98
11.	In electrochemical deposition, 0.025M $InCl_3$, 0.25 mA/cm^2, 2 min, air annealing at 120°C	undetermined	undetermined	very good	-	-
12.	Au electrochemical deposition, I=1 mA/cm^2, t=2min, air annealing at 120°C	undetermined	undetermined	very good	-	-
13.	Au chemical deposition T=2 min, air annealing at 120°C	undetermined	undetermined	very good	-	-

For the solid-state contact, after anodisation, conducting materials were formed on PS by (i) vacuum evaporation: Au, In, Au-In, In-Sn, Sn-Au, ITO, Al, Ti, Mo, Cr, Ni (2-3 A/sec and 25-30 A/sec), (ii) electrochemical deposition: Au, In, doped/undoped polypyrrole. The technological conditions were chosen in order to obtain thin, 10-20 nm metallic layers. The current densities for the electrochemical deposition processes were calculated for geometric surfaces of the samples: if the deposition takes place at the pore bottom only, current densities are the same, if the reaction takes place at the entire surface, real current densities are much lower.

3.2. Thin metallic films optical characterisation

The extinction coefficient changes with wavelength for each compound due to the changes in absorption (raising of energy states of the electrons) of the compound at different wavelengths (energy levels). A plot of the molar extinction coefficient versus wavelength will thus give a continuous curve of the wavelengths of absorption of a given compound. The extinction index values for different metals, after Johnson and Christy [24], indicate a better transmission in high energy zone, E=2-2.75 eV, (450-550 nm). It can be observed that gold is the best metal to be used as contact for the electroluminescent devices emitting in the blue zone, while chromium, and after that gold, cooper, and titanium are more suitable for the red light zone.

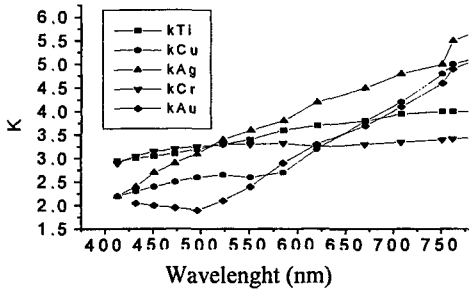

Fig. 1. The extinction index of some usual metals used as contacts on PS (after Johnson and Christy [24]).

The UV-visible transmission light of the metallic thin layer used as PS contact was determined (Fig.2). The transmission light through the investigated materials was in good agreement with the literature data [24]. It can be seen that the light transmission decreases dramatically with the film thickness; practically only very thin film, d≤10-12 nm can be used as solid contacts on PS. The In, In-Au, and In-Sn light transmission was not determined, but all these layers have good light transmission properties, even though they are thicker than 20 nm, due to their partial oxidation in air atmosphere.

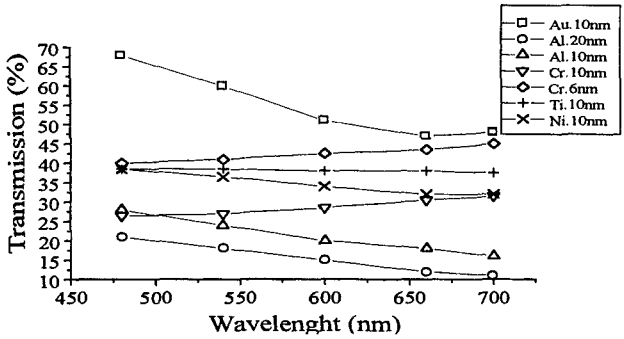

Fig. 2. The transmission spectra of vacuum evaporated metallic films, in the wavelenght interval characteristic for PS light emission.

3.3. Metal/PS structures morphology

Metal layers cover the PS layers. 80% PS layers without metallic contact (Fig. 3a) and with Au contacts on it surface (Fig. 3b) was investigated by SFM.

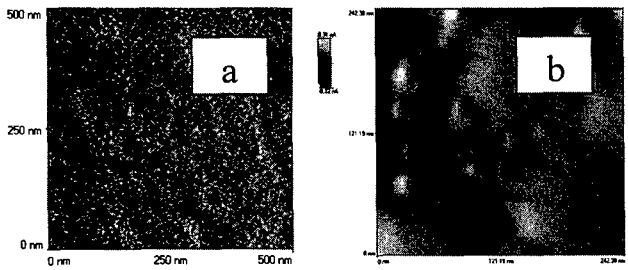

Fig 3. AFM image for 80% PS (a) and for Au/80% PS/p-Si (b)

Due to the small dimensions of PS fibrils (3-5 nm), the thin metallic film does not follow the shape of the PS surface, it is only applied on the top of the Si fibrils. However, from the SIMS spectra indicated a penetration of the metallic layer into the PS pores of about 20 nm (Fig. 4) [23].

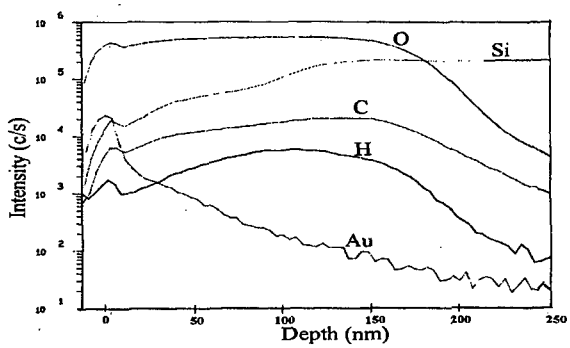

Fig. 4. SIMS depth profile of the Au/PS structure.

3.4. Electrical characterisation

To explore the mechanism of room-temperature visible EL from LED/PS, it is very important to characterize the electrical properties of the conducting material/PS interface. From the current-voltage measurements, the characteristics of the different metallic contacts / 80%PS / Si-p structures show a rectifying behavior (Fig. 5). These curves were analyzed using the thermionic emission equation.

At low injection levels (< 0.2V) the I-V characteristics are different for Al contacts and InSn, Au, and In contacts. An explanation is that the better contact metal / PS was electrochemically obtained for InSn, Au, and In compared to vacuum deposited Al. This is due to the better penetration of the pores by the electrolyte solution. The lower n values at low injection levels are due to the reduction of the interface states, as a result of the good stabilization of the PS surface. φ_b is in the same range of values: 0.83 eV (Al), 0.72 eV (InSn), 0.75 eV (Au). The best contact with lower series resistance and lower ideality factor is realized by electrochemically deposited In. These type of structures are indicated for LED on PS.

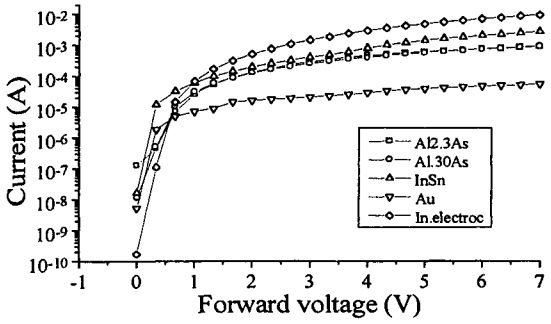

Fig. 5. I-V forward characteristics for some metallic layers used as LED solid contacts

4. Conclusions

Different thin films were investigated as the solid contact for PS electroluminescent devices. The electrical measurements demonstrated that the electrochemical processes are suitable for preparing metallic contacts on PS electroluminescent devices. The gold represents the best choice due to its high light emission transmission, on the whole wavelength light emission domain of the PS. Also, good results were obtained using electrochemical In and vacuum deposited In-Sn contacts, annealed in air at 120^0C.

Acknowledgements

The authors acknowledge the support of the European Community through the INCO-COPERNICUS program, contract SBLED No. 7037 / 1998 and the support of the National Agency for Science, Technology and Innovation.

References

1. Canham , L. T. (1990) Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, *Appl. Phys. Lett.* 57, 1046-1049.
2. Richer, A., Steiner, P., Kozlowski, F. and Lang, W. (1991) Current induced light emission from porous silicon device, *IEEE Electron Dev. Lett.* 12, 691.
3. Koshida, N. and Koyama, H. (1992), Visible electroluminescence from porous silicon, *Appl. Phys. Lett.* 60, 347-350.
4. Steiner, P., Kozlowski F. and Lang, W. (1993) Blue and green electroluminescence from a porous silicon device, *IEEE Electron Device Letters*, vol. 14, no. 7, 317-319.
5. Lang, W. (1998), Porous silicon Electroluminescent Devices in G. Amato, C. Delerue, H. J. Bardeleben, (eds.), *Structural and Optical Properties of Silicon Nanostructures*, Gordon and Breach Science Publishers, pp. 539-555.
6. Cox T. I. (1997), Electroluminescence from porous silicon using solid state contacts, in L. Canham (ed.), *Properties of porous Silicon,* EMIS Datareviews Series No. 18, Published by INSPEC, IEEE London, UK, pp. 290-310.
7. Muraska, H. P., Namavar, F., Kalkhoran, N. M., (1992) Visible electroluminescence from porous silicon np heterojunction diodes, *Appl. Phys. Lett.* (USA), vol. 61, 2514.
8. Kozlowski, F., Steiner, P., Lang, W. (1993) Electroluminescence from porous silicon in D. C. Bensahel, L. T. Canham, S. Ossicini (eds), *Optical properties of low dimensional silicon structures*, Proc. NATO-ARW, Series E, Applied Sciences, vol. 244, 123-132.
9. T. Oguro, H. Koyama, T. Ozaka, N. Koshida (1997) Mechanism of the visible electroluminescence from metal/porous silicon /n-Si devices, *J. Appl. Phys.* (USA) vol. 81 1407-1412.
10. Steiner, P., Wiedenhofer, A., Kozlowski, F., Lang, W., (1996), Influence of different metallic contacts on PS electroluminescence, *Thin Solid Films*, vol. 276, 159-163.
11. Lazarouk S., Bondarenko V., Jaguiro P., Lacquaniiti N., Maiello G., La Monica S., Masini G., Ferrari A. (1996) Electrical characterization of visible emitting electroluminescent Schottky diodes based on n-type porous silicon and on highly doped n-type porous polysilicon , *Journal of Non-Crystalline Solids*, v.198-200, 973-976.
12. Lazarouk, S., Jaguiro, P., Katsouba, S., Prohorenko, A., Masini, G., La Monica, S., Maiello, G., Ferrari, A. (1996) Silicon-based optical interconnections, MRS Symposium Q, *Advances in Microcrystalline and Nanocrystalline Semiconductors*, 2 - 6.
13. Jaguiro, P., La Monica, S., Balucani, M., Lazarouk, S., Maiello, G,. Masini, G., Ferrari, A. (1997) Characterization of Porous Silicon Light Emitting Diodes in High Current Density Conditions, *Solid State Phenomena,* Vol. 54, 21-26.
14. Lazarouk, S., Jaguiro, P., Katsouba, S., Masini, G., La Monica, S., Maiello, G., Ferrari, A., (1996) Stable electroluminescence from reverse biased n-type porous silicon-aluminum Schottky junction device, *Appl. Phys. Lett.*, vol. 68, 2108-2110..
15. Lazarouk, S., Jaguiro, P., Katsouba, S., La Monica, S., Maiello, G., Masini, G., Ferrari, A. (1996) Visible light from aluminium-porous silicon Schottky junctions, *Thin Solid Films,* vol. 276, 168-170.
16. Gosele, U. and Lehmann, V. (1994), Porous silicon, Porous Silicon Quantum Sponge Structures: Formation Mechanism, Preparation Methods and Some Properties, in Z. C. Feng and R. Tsu (eds.), *Porous silicon*, World Scientific, Singapore, p. 17.
17. Bsiesy, A., Muller, F., Ligeon, M., Gaspard, F., Herino, R., Romenstain, R. and Vial J. C. (1994) , Voltage-tuned electroluminescenceof porous silicon, *Appl. Phys. Lett.*, 65, 3371-3374.
18. Steiner, P. Kozlowski, F. Wiedenhofer, A. Knoll, B. Lang, W.(1996) Fabrication and performance of electroluminescent porous silicon devices, *Proceedings of the International Symposium on Advanced Luminescent Materials*, 48-57.
19. Lang, W., Kozlowski, F., Steiner, P., Knoll, B., Wiedenhofer, A., Kollewe, D., Bachmann, T., (1997) Technology and RBS analysis of porous silicon light-emitting diodes, *Thin Solid Films,* vol. 297, no. 1-2, 268-271.
20. Lang, W., Steiner, P., Kozlowski, F. (1994) Optoelectronic properties of porous silicon-The electroluminescence devices, in J. C. Vial, J. Derrien (eds), *Porous silicon science and technology*, Springer-Verlag, Les Editions de Physique, pp. 293-305.
21. Aylett, B. J., Harding, I. S., Earwarker, L. G., Forcey, K., Giaddui, T. (1996) Metallisation of PS by chemical vapour infiltration and deposition, *Thin Solid Films,* 276, 253-256.
22. Matsumoto, T., Minura, H., Kanemitsu, Y. (1995) Photo- and electroluminescence from electrochemically polished silicon, *Jpn. J. Appl. Phys*, vol 34, , nr. 10B, L.1318-L1321.

23. Kleps, I., Angelescu, A. (1998) Porous silicon: material processing, properties and applications in light and field emission devices, *Romanian Journal of Information Science and Technology*, vol 1, nr. 2, 167-182.
24. Johnson, P. B. and Christy, R. W. (1972) Optical constants of noble metals, *Phys. Rev. B*, 6, 4370.